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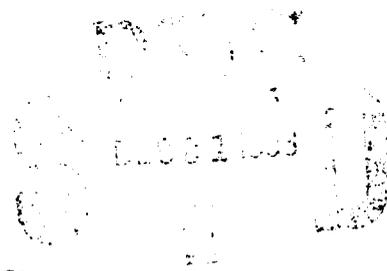
Synthesis of Gram Quantities of C₆₀ by Plasma Discharge in a Modified Round-Bottomed Flask. Key Parameters for Yield Optimization and Purification

by

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Synthesis of Gram-Quantities of C₆₀ by Plasma Discharge in a Modified Round-Bottomed Flask. Key Parameters for Yield Optimization and Purification

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Abstract

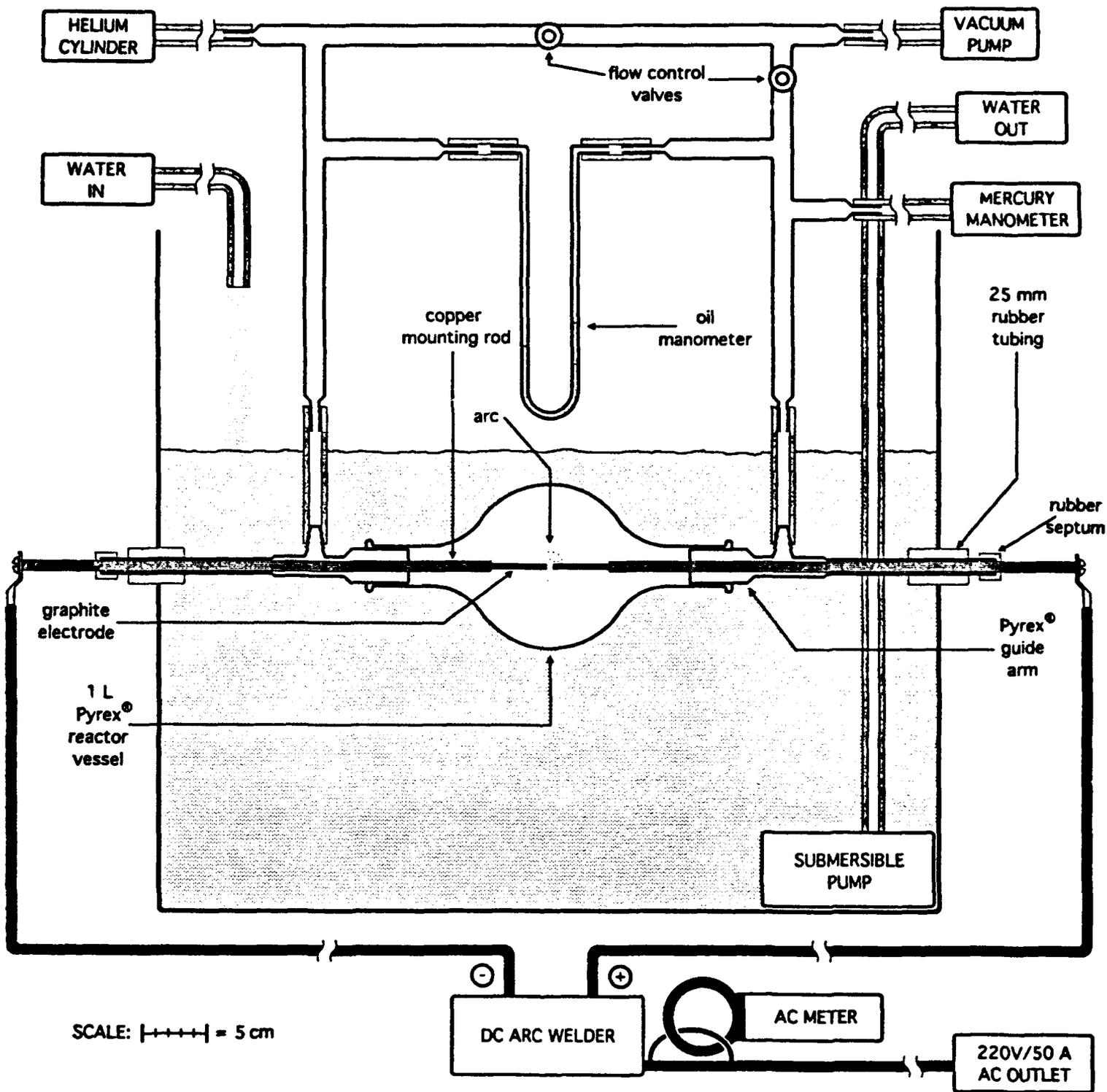
Described is the fabrication of a plasma discharge reactor constructed from a 1 L round-bottomed flask that allows for the preparation of gram-quantities of C₆₀ in an eight hour period. The modified reactor design (1) is inexpensive (2) requires almost no machining (3) has high thru-put (4) affords high yields of fullerenes (5) allows one to have near continuous feed of graphite rods and (6) permits control over four major reaction parameters important for the clean formation of fullerenes. The four major reaction parameters necessary to control for the high yield of fullerenes are the absolute pressure, the rate of helium gas flow through the reactor, the current level of the arc as determined by the setting on the arc welding unit, and the arc gap maintained by monitoring the current on a clip-on digital AC current meter. Since the apparatus described can allow for easy adjustment of all four major reaction parameters, this design could also be used to study the changes in fulleroid content based on parameter modification. Also detailed is the efficacy of a procedure for the purification of the crude fullerene mixtures using activated charcoal as a chromatographic stationary phase.

Since the initial discovery of buckminsterfullerene (C_{60}) in 1985¹ and the subsequent development of the carbon arc method for producing macroscopic quantities of this material,² a large amount of effort has been directed toward the understanding and utilization of this new allotrope of carbon.³ We describe here the fabrication of a plasma discharge reactor constructed from a 1 L round-bottomed flask that allows for the preparation of gram-quantities of C_{60} in an eight hour period. The reactor design (1) is inexpensive (2) requires almost no machining (3) allows high thru-put (4) affords high yields of fullerenes (5) allows one to have near continuous feed of graphite rods and (6) permits control over four major reaction parameters important to the clean formation of fullerenes. Since the apparatus described can allow for easy adjustment of all four major reaction parameters, this design could also be used to study the changes in fulleroid content based on parameter modification. We also detail the efficacy of a procedure for the purification of the crude fullerene mixtures using activated charcoal as a chromatographic stationary phase.

The most common method of producing C_{60} utilizes the Huffman-Krättschmer carbon arc method in which graphite electrodes are vaporized in a low pressure helium atmosphere by passing an electrical current through the electrodes, thus generating an arc. The soot produced by this carbon arc contains C_{60} as well as some other higher molecular weight fullerenes. A number of reports on this method have appeared that provide details of the apparatus used.^{4,5} There are two major variants of the carbon arc method, namely, contact arc and plasma discharge. In the contact arc method, the graphite electrodes are kept in constant contact through either a gravity feed mechanism^{4b} or through the use of a feed spring.^{4c,e} To date, the most easily accessible apparatus for the contact arc method is the gravity feed apparatus developed by Wudl.^{4b} This is a relatively inexpensive and simple device which uses an arc welder as the power source. However, like all other contact arc apparatus, it

suffers from overheating problems due to resistive heating of the graphite electrodes and the apparatus must be disassembled for the insertion of new graphite rods. The plasma discharge method^{4a,d} maintains a constant arc gap between the electrodes, thus avoiding much of the resistive heating problems found in the contact arc methods. This method can potentially produce crude fullerenes more efficiently by providing more control over the conditions which form the fullerenes in the reactor. The drawback to the plasma discharge method is that it requires a fairly complex apparatus with special feed mechanisms to align the electrodes and maintain a constant arc gap. And, like most other methods, the apparatus must be disassembled for the insertion of new graphite rods.

Here we describe the simple fabrication and use of a low cost fullerene generator of the plasma discharge type (Figure 1). The reaction vessel is simply a 1 L Pyrex[®] round-bottomed flask that has had an additional 24/40 female joint affixed opposite to the first joint. The Pyrex[®] guide arms (12 mm outside diameter) extend from outside the water cooling bucket and are fitted with vacuum take off adapters and tipped with 24/40 male joints that insert into the reactor vessel (the total length of the guide arm including the male joint is 25 cm). The guide arms help to align the 1 cm diameter copper mounting rods (each copper mounting rod is 35 cm long). One end of the copper mounting rods has a 3/16" diameter hole drilled to a 1 cm depth for mounting the graphite electrodes and on the other end has a screw hole tapped so that the rods can be attached to the arc welder with brass screws. The copper mounting rods extend out through the end of the guide arms and through standard 19/22 septa which have a #2 hole punched through their center. These septa maintain a seal between the sliding copper mounting rod and the end of the Pyrex[®] guide arm. The guide arm's vacuum take off adapters connect, via rubber tubing, to a gas manifold mounted above the reactor vessel (the outside diameter of the manifold tubing is 15 mm).



The entire vessel, except for the ends of the guide arms, is submerged in a cooling water bath made from a plastic storage container.⁶ Two holes slightly less than 25 mm in diameter are made in the side of the storage container by heating an appropriately-sized glass tube in a gas flame and melting through the plastic. It is through these holes that the guide arms pass while water leaks are prevented by using rubber gaskets made from a short lengths of 25 mm rubber tubing. A submersible water pump is placed at the bottom of the cooling bath which helps to circulate the cooling (tap) water around the vessel and allows the water to be removed from the bath as quickly as it flows in from a rubber hose at the top of the bath. If the water is not circulated and replenished in this manner, the bath tends to overheat which can result in the vessel cracking.

The gas manifold above the vessel carefully monitors and controls the atmospheric conditions inside the vessel. Helium flows into the left side of the manifold and the gas is removed from the right side of the manifold by a vacuum pump. The absolute pressure of gas in the vessel is monitored by a mercury manometer mounted on the right side of the manifold just above the reactor vessel. The pressure difference between the two sides of the vessel is an indication of the direction and magnitude of gas flow through the vessel and is measured by a silicon oil manometer (8 mm outside diameter) mounted across the two sides of the manifold. The flow of the gas through the reaction vessel is controlled by two standard high vacuum Teflon[®] plug control valves. The central valve acts as a shunt, directing all or some of the helium flow through the vessel rather than across the top of the manifold. The valve on the right side of the manifold controls the rate of helium flow out of the vessel and thus regulates the sensitivity of the shunt control valve.

The reactor is powered by a variable current AC/DC arc welder which is plugged into a standard 220 V/50 A wall outlet.⁷ A clip-on digital AC current meter is attached to the input end of the arc welder to monitor the current.⁸

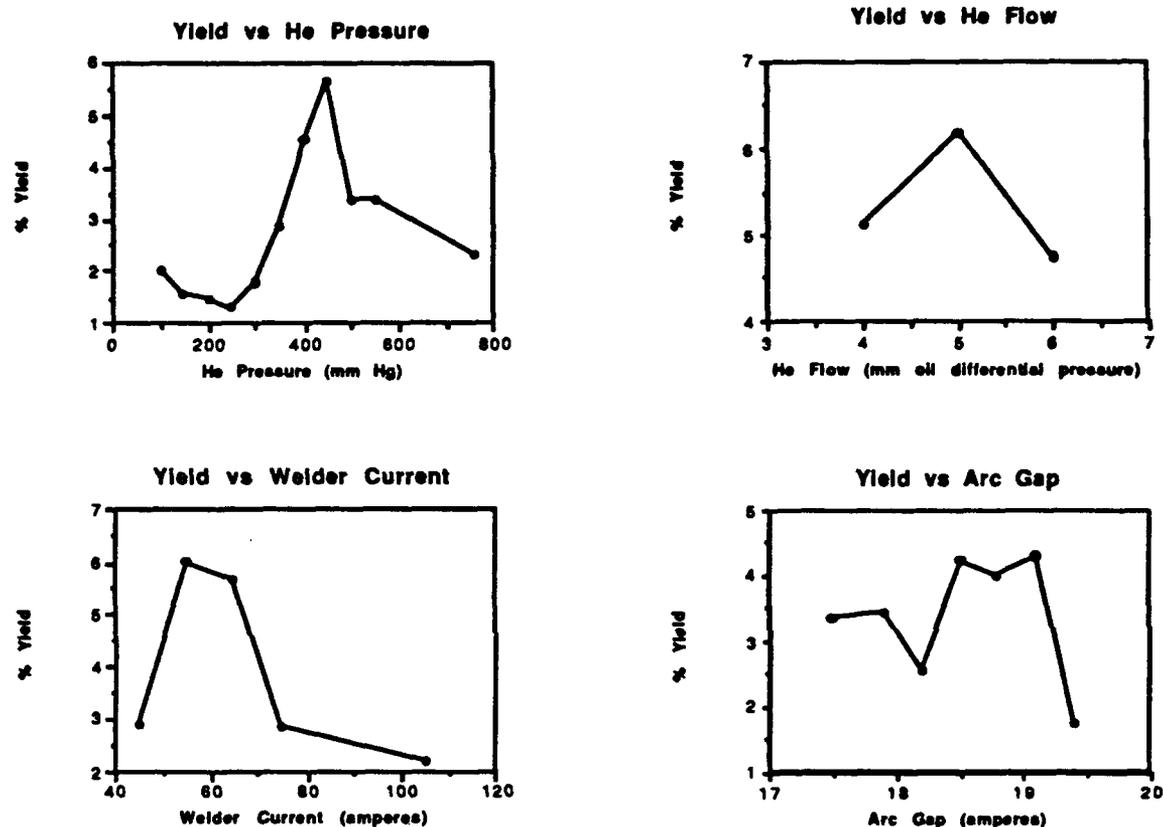
The apparatus described not only provides us with an inexpensive and easily fabricated fullerene reactor, but it also gives us the flexibility to adjust and optimize various reaction parameters in order to increase yields. We have determined that there are four easily adjusted parameters that must be maintained for high yields: (1) the absolute pressure, (2) the rate of helium gas flow through the reactor, (3) the current level of the arc as determined by the setting on the arc welding unit, and (4) the arc gap maintained by monitoring the current on the clip-on digital AC current meter. Other workers have dealt with some of these parameters but here we describe the control and optimization of all four parameters simultaneously (Figure 2). Optimization studies were done with inexpensive graphite welding electrodes.⁹ We eventually started using high purity graphite electrodes which doubled our yields.¹⁰ Even with this change in electrode type, all the optimized reactor conditions given in Figure 2 hold for both sources of graphite except for the optimal arc gap measured in amperes on the clip-on digital AC current meter.

Helium pressure is the operating parameter that is commonly reported for the synthesis of fullerenes. Our studies have shown that there is a local yield maximum at about 150 mm Hg but that the yield optimum occurs at 450 mm Hg after going through a yield minimum at 250 mm Hg. An optimized operating pressure of 450 mm Hg is significantly higher than the operating pressures of 100-200 mm Hg normally used by other workers;³ however, a recent report suggested that optimal pressures for graphitic nanotube formation was in the range of 500 mm Hg, similar to our maximum for C₆₀ formation.¹¹ These pressures are monitored by a standard U-shaped mercury manometer and the pressures can be accurately adjusting by the low-pressure valve on the helium regulator.

The next condition that we investigated was that of helium flow through the reactor. By adjusting the flow control valves on the gas manifold and monitoring the differential pressure on the U-shaped silicon oil manometer, one can adjust the

Figure 2

Parameters versus yield of crude extractable fullerenes



helium flow through the reactor from 0 mm (a static helium atmosphere) to greater than 30 mm oil pressure. A differential oil pressure reflects a net helium flow through the reactor from left to right. An optimum flow was found at 5 mm oil pressure. Pressures greater than 6 mm caused the soot to accumulate on the right side of the reactor and blew soot out of the reactor and into the manifold and vacuum lines. Pressures less than 4 mm gave extremely low yields and caused the soot to accumulate on the left side of the reactor. Observation of the arc through a modified reactor vessel equipped with a view port¹² revealed that under a static helium atmosphere the arc plume actually flowed from the positive to the negative electrode

(this is the direction of the current flow). A slight helium flow in the opposite direction seemed to counteract this current flow and "balanced" the arc so that at the optimum flow of 5 mm, the soot stayed in the center of the reactor vessel rather than flowing out one side or the other.

The welder current was the next parameter that we investigated and it was adjusted to obtain an optimum fullerene yield. Our studies showed that a current of 55 A gave the best yields. Higher currents increased graphite rod burn rates but decreased yields.¹³ At currents lower than 55 A we had difficulty maintaining an arc.

Finally, varying arc gaps were investigated. Other workers optimized this parameter by setting the arc gap to a level where the arc was "brightest".¹⁴ We sought to find a more objective criteria for determining arc gap and found that monitoring the current draw of the arc with the clip-on digital AC current meter attached to the arc welder was a convenient and reliable way of monitoring this parameter.⁸ While using welding grade graphite rods,⁹ an optimum arc gap of 2-4 mm (determined visually through the view port)¹² corresponded to a current reading of 18.5-19.0 A on the clip-on digital current meter. Using high purity graphite rods,¹⁰ an the optimum arc gap of 2-4 mm corresponded to a current reading of 6.6-7.2 A on the clip-on digital current meter.

A detailed experimental procedure is as follows. The two guide arms were removed from a 110°C oven, the 25 mm rubber tubing gaskets were slipped onto the end of the arms, the manifold hoses were attached and the two arm assemblies were inserted through the holes of the empty cooling bath. The reactor vessel was then removed from the oven, the two joints were well-lubricated with silicon grease, and the vessel was mounted between the two guide arms. Adjustments in the guide arms were made to ensure a tight fit between the ground glass joints. Two weighed high purity graphite electrodes¹⁰ (6" long) were inserted into the ends of the two copper

mounting rods, the rubber septa were slipped over the other ends of the rods, and the rod assemblies were then inserted into the end of the guide arms. The septa were adjusted so that they slip over the end of the guide arm and give a reasonable vacuum seal.¹⁵ The chamber was then evacuated, and the reactor was attached to the arc welder with the screw connections. The cooling bath was filled with tap water and the water flow was adjusted so that when the submersible pump was turned on, there was no net flow of water out of the cooling bath. It is important that the reactor vessel is always covered with water to avoid cracking of the reactor. The system was then kept under 5 mm vacuum¹⁵ for 20 minutes. Helium was then introduced into the reactor and the pressure was adjusted at the regulator until an absolute pressure of 450 mm Hg was obtained as determined by the mercury manometer. The flow control valves were then adjusted until a differential pressure of 5 mm was reached in the silicon oil U-tube. The copper mounting rods were pushed in until the two graphite rods were centered in the vessel but were not touching. While wearing rubber gloves and welder's goggles, the arc welder was set to 55 A DC, and the AC current meter and the arc welder were turned on (*CAUTION*).¹⁶ The right copper mounting rod was pushed in slightly so that the graphite electrodes briefly touched and established an arc. This right copper rod was then moved in or out until the current meter read 7.2 A. The rod was allowed to burn until the current meter read 6.6 A at which point the right copper rod was again pushed in until a 7.2 A reading was obtained. This process was then repeated. One only needs to adjust the right copper rod (the positive electrode) because the left electrode is never consumed. It takes from 2-3 minutes for the graphite rod to burn through the 7.2-6.6 A range. Slag (as observed through the view port of our test apparatus)¹² accumulates on the left electrode and must occasionally (about every 30 minutes) be removed. This is accomplished by turning off the arc welder, waiting 30 seconds for the electrodes to cool, and tapping on the left copper mounting rod with a glass rod which knocks the

slag off the electrode. Failure to turn off the arc welder and wait for the electrodes to briefly cool before dislodging the slag can cause the vessel to crack when the hot slag hits the bottom of the vessel and induces thermal stresses in the glass. An entire 15 cm electrode was consumed in about 1.25 hours. One must be careful to not burn the graphite rod down below 1.5 cm; failure to do this can cause the arc to jump to the copper mounting rod, melting the top of the copper rod and necessitating redrilling of the graphite rod holding hole. Additional graphite electrodes can be burned in the same run by turning off the welder, bringing the reactor up to atmospheric pressure, removing the right mounting rod and replacing the consumed graphite stub with a new rod, re-inserting the mounting rod, pumping the system down to 5 mm Hg, bringing the atmosphere back to 450 mm Hg, turning the welder back on, and initiating a new arc. One need not disassemble the apparatus nor empty the cooling bath during this procedure. About six rods can be consumed in an eight hour period. If more than eight rods are consumed in a single run, the guide arms tend to clog with soot and the reactor becomes inefficient.

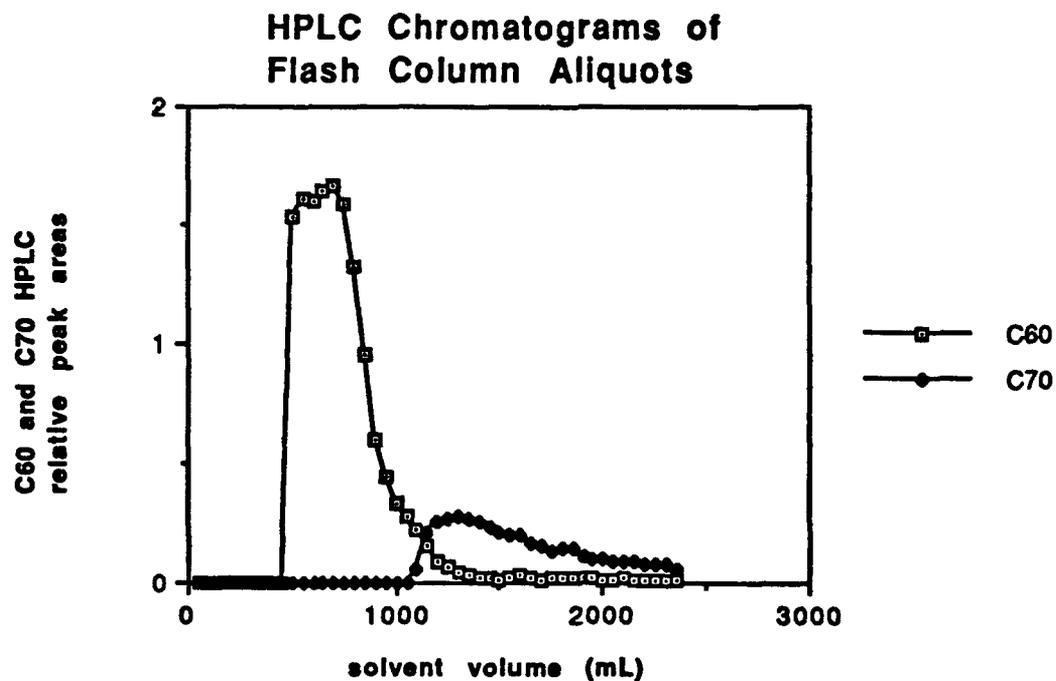
When the run was complete, the reactor was taken apart and the vessel had the joints wiped free of grease with paper towels and hexane. One end of the vessel was capped with a 24/40 rubber septum, the flask was filled with 500 mL of toluene, and then the other end of the vessel was also capped with a 24/40 rubber septum which had a needle inserted in it to avoid pressure build-up in the vessel. The reaction vessel was then carefully shaken to dislodge most of the soot and facilitate suspension of the soot in the toluene. The vessel was then placed in a sonic water bath for 30 minutes (with the needle pointing up and out of the water). The black soot suspension was then filtered through a pad of Celite[®]-521 in a fritted glass funnel to give a dark red-brown solution of crude fullerenes. The solvent was removed from the crude fullerene extract by rotary evaporation to give a black powder. The black powder was suspended in diethyl ether and poured onto the top of a small plug of

silica gel. The crude fullerenes are insoluble in ether and stay at the top of the column. While at the top of the column, the crude material was washed generously with ether and then flushed through the column with distilled toluene. The discarded ether washings removed the grease residues and the ubiquitous hydrocarbon side-products of the fullerene reaction; the silica gel plug also acts as a fine filter to remove any soot that passed through the Celite® pad. This filtered crude extract was then concentrated by rotary evaporation and weighed. We have found that this clean-up procedure is necessary for obtaining accurate weights of the crude soluble fullerene extracts and neglect of this type of purification will undoubtedly cause hydrocarbon and/or insoluble particulate to inaccurately enhance the reported crude yields. The weights of the consumed rods and the slag were obtained and subtracted from the initial weights of the rods to give a weight of the graphite that was consumed and converted into soot. The crude yield was then calculated from these values. A typical 1-rod run takes 78 minutes, burns 2142 mg of graphite, and produces 278 mg of soluble crude fullerenes giving a crude yield of 13%. Yields reproducibly ranged from 11-14%. Thus an eight hour run that consumes six graphite rods will produce ~1.7 g of crude fullerenes from which ~1.0 g of pure C₆₀ can be obtained by the below purification procedure.

The crude material was purified on an activated charcoal/silica gel flash column.¹⁷ A slurry of alkaline decolorizing carbon Norit®-A (36 g) and silica gel (72 g) in toluene (200 mL) was poured into a typical glass flash chromatography column (38 mm diameter and 40 cm long) that had a cotton plug at the bottom of the column. The slurry was allowed to settle as the solvent *above* the stationary phase was allowed to drain under a 7.5 psi N₂ head pressure applied at the top of the column.¹⁸ The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. A saturated toluene (400 mL) solution of crude fullerenes (1.85 g) extracted from carbon arc soot was slowly poured onto the top of the Norit®-

A/silica gel stationary phase. A 7.5 psi N₂ head pressure was applied thus providing a ~16 mL/min elution rate. The deep purple-colored solution containing C₆₀ started to elute from the column after 37 min. After 36 min more, the eluant was only faintly purple and collection of a second fraction was then begun. The total volume of toluene needed for obtaining the C₆₀ fraction (first fraction) was ~600 mL. After 3 min more, a red-brown band characteristic of C₇₀ started to elute. A graph of aliquots analyzed by HPLC¹⁹ shows the relative concentrations of C₆₀ and C₇₀ versus solvent volume (Figure 3). Removal of the solvent from the purple fraction afforded

Figure 3



1.16 g of crystalline C₆₀ (63% of a possible 75% of C₆₀ in extractable fullerenes) that was >99% pure by HPLC.^{17,19} This represents a net yield of about 8.5% pure C₆₀ based on the weight of the graphite consumed.²⁰ While the second band eluted from the

column was red-brown, it did contain some C₆₀. One more smaller chromatographic run on the initial red-brown portion afforded 74 mg more of C₆₀ and 120 mg of a sample that was ~1 : 10 in C₆₀ : C₇₀ as judged by HPLC analysis.¹⁸ Thus the combined yield of purified C₆₀ after two columns was 67% of a possible 75% of C₆₀ in extractable fullerenes.

Although we illustrated this purification procedure with 1.85 g of extractable fullerenes, it worked equally well on a smaller scale using the proportionately smaller stationary phases and solvent volumes. Norit[®]-A alone as the stationary phase without silica gel as a co-phase worked excellently for C₆₀ separations on smaller scales (i.e., 100 mg of crude fullerenes with 2.0 g of Norit[®]-A); however, the silica gel prevents cracking of the stationary phase in the larger columns and allows for higher flow rates.

In summary, we have described an inexpensive and easily fabricated fullerene reactor of the arc discharge type. The apparatus described allows one to control various reaction parameters and optimization of the parameters gives reproducible runs of 11-14% crude yield. The crude material is purified on an activated charcoal/silica gel column to give a net pure C₆₀ yield of 8.5% from consumed graphite.²⁰

Acknowledgements. This research was funded by the Department of the Navy, Office of the Chief of Naval Research, Young Investigator Award Program (1989-92), the National Science Foundation (RII-8922165, DMR-9158315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96) for JMT: Hercules Incorporated, IBM Corporation, Ethyl Corporation, and the Shell Development Company. WAS thanks NASA and the American Vacuum Society for scholarships. We thank Dr. Nick Griffith of the Aluminum Company of America for providing us with alumina for the comparison studies.

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(5) There are other methods of producing C₆₀, most notably from hydrocarbon flames and by the thermal evaporation of carbon, see: (a) Howard, J. B.; McKinnon, J. T.; Makarovskiy, Y.; Lafleur, A. L.; Johnson, M. E. *Nature* 1991, 352, 139. (b) Peters, G.; Jansen, M. *Angew. Chem. Int. Ed. Engl.* 1992, 31, 223.

(6) These storage containers are available at most department stores for approximately \$10 and are made of a flexible plastic similar to plastic garbage containers.

(7) The arc welder (Lincoln Electric model AC/DC 225/125) was purchased from a local welding supplier and cost approximately \$300.

(8) The clip-on digital AC current meter was purchased from a local electronics distributor for approximately \$100. The meter is attached around one of the two hot leads of the 220 V power cord attached to the arc welder. One can access these leads by carefully removing the outer power cord covering, exposing three wires, namely, the two colored hot leads and the one white ground lead. Care must be taken to not penetrate the insulation of these inner wires. The current meter is then clipped around one of the exposed hot leads. The metallic portion of the wires should never be exposed.

(9) Standard 3/16" copper clad graphite electrodes (Arcair brand, \$0.25/rod) were obtained from a local welding supply center. The copper sheathing was peeled off before use. Technical data sheets on these electrodes showed that a significant amount of the mass consisted of non-graphitic binders that probably caused the lower yields seen in the optimization study graphs.

(10) High quality graphite electrodes (Cat. #AXF-5Q1, \$1.92/rod, 6" long, 3/16" diameter) were obtained from Poco Graphite, Inc., 1601 South State Street, Decatur, Texas 76234.

(11) Ebbesen, T. W.; Ajayan, M. *Nature* 1992, 358, 220.

(12) The apparatus with a view port had an additional 24/40 female joint placed at right angles to the guide arms in the center of the 1 L reaction vessel, directly above the point of the arc. A tube was made with a male 24/40 joint (20 mm diameter, 20 cm long tube including the male joint) at one end and a clear glass window attached to the tube with epoxy at the other end. This tube was inserted into the

female joint such that the window points up and out of the water bath. It is through this window that we directly observed the arc. Welder's goggles are used when looking into the port at the arc to avoid eye injury. Use of a view port of this type will easily allow observation of electrodes and slag build-up.

(13) Wudl *et al.* had similar burn and yield observations when moving to a higher current. See ref 4b.

(14) Parker *et al.* observed that their optimum arc gap was 4 mm. See ref. 4a.

(15) With our apparatus a vacuum of only 5 mm Hg can be obtained. The rubber septa are most likely the weak points in our system and cause the leaks which prevents us from obtaining lower pressures.

(16) The apparatus poses risks of electrical shock similar to those risks incurred during ordinary arc welding. Accordingly, rubber gloves should be worn to avoid electrical shock while handling the exposed copper rods. The operator should wear rubber-soled shoes and only one hand should be in contact with the copper rod at any time. To avoid eye injury, welder's goggles should be worn when observing the arc.

(17) Alkaline decolorizing carbon Norit[®]-A was purchased from Fisher Scientific Company. Flash chromatography grade Silica Gel 60 (230-400 mesh ASTM, 0.040-0.063 particle size) was purchased from EM Science. A detailed description of this purification method and the purity of the C₆₀ and C₇₀ obtained was recently described. See: Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* in press.

(18) **CAUTION:** Though we experienced no rupture of the glass under 7.5 - 10 psi pressures, we recommend utilization of this procedure behind a protective transparent shield to prevent injury if a rupture should occur.

(19) HPLC was done using an Alltech Econosphere silica gel column (250 mm x 4.6 mm I.D.) with 2% toluene in hexane at 1 mL/min using UV detection at 284 nm. The crude material showed a mixture of C₆₀, C₇₀, C₈₄, and possibly other higher

fullerenes in a peak area ratio of 58.0, 38.9, 1.6, and 1.5, respectively. The retention times were 5.1, 5.9, 6.6, and 7.4 min, respectively, with baseline separation. Thus, at 284 nm, the extinction coefficient of C₇₀ appears to be greater than that of C₆₀ therefore skewing detection in favor of C₇₀.

(20) In summary, 2,142 mg of graphite consumed from one rod yields 278 mg of crude fullerenes = 13% (generally 11-14%) crude yield or yield of soluble extract. At 2,142 mg of graphite consumed per rod x 6 rods per 8 h = 12.9 g of graphite that can be consumed in this apparatus per 8 h. 12.9 g of graphite consumed x (11% to 14% crude yield) = 1.42 to 1.81 g of crude fullerenes per 8 h. 1.42 g to 1.81 g x 63% chromatographic recovery of pure C₆₀ = 0.89 g to 1.14 g of pure C₆₀. 0.89 g to 1.14 g of pure C₆₀/12.9 g of graphite consumed = 6.9% to 8.8% of pure C₆₀ obtainable based on the mass of graphite consumed.